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54   Title: Procedure to prepare organic fluorine compounds

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<u>Patent Claims:</u>

1.   Procedure to prepare organic fluorine compounds by reacting the corresponding halogen compounds (that are substituted in at least one position by a halogen different from fluorine) with fluorides of nitrogenous bases, characterized in that the fluorides of nitrogenous bases are hydrofluorides of organic nitrogenous bases.

2   Procedure according to claim 1, characterized in that the starting halogen compounds that are substituted at least one position by a halogen different from fluorine are organic chlorine and/or bromine compounds.

3.   Procedure according to claims 1 and 2, characterized in that the starting halogen compounds that are substituted at least one position by a halogen different from fluorine are chloroalkanes and/or bromoalkanes, (α-ethylene chloride and/or (α-ethyl bromide, (α-chloro and/or (α-bromoketone, (α-chloro and/or (α-bromocarboxylic acid ester, carboxylic acid chloride and/or bromide, and chlorine and/or bromine aromates and/or heterocycles.

4.   Procedure according to claims 1 - 3, characterized in that the hydrofluorides of organic nitrogenous bases are the hydrofluorides or primary, secondary, and/or tertiary (preferably secondary and/or tertiary) aliphatic amines with up to 12 C atoms.

5.   Procedure according to claims 1-4, characterized in that when hydrofluorides of organic nitrogenous bases are used that have more than one molecule of hydrofluoride per molecule of organic nitrogenous base, the reaction is carried out in the presence of a basic solvent, preferably a N-(C1-C4)-alkyl-substituted C5- and/or C6-lactam.

6.   Procedure according to claims 1-5, characterized in that the reaction is carried out at temperatures between approx. -10 to +150°C.

Procedure to Prepare Organic Fluorine Compounds

Organic fluorine compounds are, for example, important as potential inhalation narcotics and as intermediate products for the synthesis of valuable end products such as reactive dyes, pesticides, etc.

There is a series of known methods to prepare them; one of the most important is to exchange halogen atoms in the corresponding halogen compounds with fluorine. An overview of such procedures is e.g. found in: Houben-Weyl, Methoden der Organischen Chemie, Vol. V/3, (G. Thieme Verlag: Stuttgart, 1962), and in: M. Hudlicky, Chemistry of Organic Fluorine Compounds, 2nd Ed., (1976), Ellis Harwood Ltd.

Depending on the type of compound and the reactivity of the chlorine, bromine or iodine atom to be exchanged, either gaseous hydrogen fluoride is used as the fluorinating agent (for example in reaction ovens on solid catalysts) or liquid hydrogen fluoride (for example in autoclaves in the present antimony salts). An example of using hydrogen fluoride as the fluorination agent is the preparation of cyanuric fluoride from cyanuric chloride with hydrogen fluoride at -78°C with subsequent fractionation (G.A. Olah, M. Nojima, I. Kerekes, Synthesis, (1973) p.487). A substantial amount of equipment and safety precautions are necessary to carry out the reaction on a relatively small scale since, of course, working with free hydrogen fluoride always requires substantial safety measures.

Alkali fluorides and ammonium fluoride are also used as fluorinating agents. According to Hudlicky, their reactivity can be graded as follows:

$CsF > RbF > KF > NaF > NH_4F > LiF$
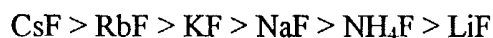
Accordingly, cesium and rubidium fluoride have the greatest fluorinating reactivity in this series. However, these substances are also the most expensive. The cheaper sodium and ammonium fluoride and lithium fluoride (which is also not very expensive) are not reactive enough (especially the two last fluorides). Potassium fluoride therefore is the most practical taking into consideration reactivity and price of the alkali fluoride series including ammonium fluoride.

Very frequently, uneconomical, low yields of the desired organic fluorine compounds are attained using potassium fluoride as the fluorinating agent for corresponding organic halogen compounds.

Accordingly, fluoroacetone from bromoacetone with potassium fluoride in glycol form only produces 25% of the theoretical yield (H. Machleidt, Leibigs Ann. Chem., 667 (1963) p.24).

The methods recommended in US PN 3,769,434 to prepare monofluoromethyl ethers from monochloromethyl ethers with potassium fluoride in N-methylpyrrolidone cannot be used to convert sensitive ethers or only produce very small yields; the method is largely unsuccessful for example when attempting to prepare the sensitive cyclopropyl monofluoromethyl ether
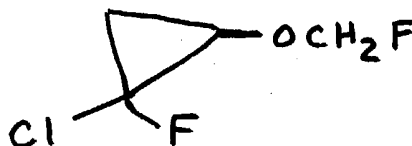
from the corresponding monochloromethyl ether. Perhaps the failure of this method to convert and prepare sensitive ethers is because relatively high temperatures are required to bring to a reaction the inorganic fluoride that is relatively scarcely-soluble in N-methylpyrrolidone and whose particle size plays a large role. The relatively high temperatures frequently cause the substrate and the product to decompose and also require a rather large amount of energy.

Other inorganic fluorinating agents are the fluorides of e.g. silver, mercury and antimony. Primarily their relative inaccessibility and hence high cost prevent their use on a large industrial scale.

Beyond the cited pure inorganic fluorination agents, there are fluorinating agents that are at least partially organic in character. Such fluorinating agents are for example tetraalkylammonium fluoride (see J.-F. Normant, J. Bernadin, Compt. Rend. Ser. C., 296 (1969) 2352). These compounds are, however, relatively inaccessible and hence rather expensive like the cited silver, mercury and antimony fluorides.

Due to the various disadvantages of the prior art fluorination agents and methods, it was hence desirable to solve the problem of finding a fluorination method and/or agent without these disadvantages. In particular, working with large amounts of free hydrofluoric acid was to be avoided; in addition, the new agent or method should be easily accessible and hence economical and useful for preparing sensitive fluorinated substance. This problem was easily solved according to the invention by using hydrofluorides of organic nitrogenous bases as the fluorinating agent.

The subject of the invention is hence a process to prepare organic fluorine compounds by reacting the corresponding halogen compounds (that are substituted at least one position by a halogen different from fluorine) with fluorides of nitrogenous bases; the process is characterized in that the hydrofluorides of organic nitrogenous bases are used as the fluorides of nitrogenous bases.

In principle, any organic starting halogen compounds can be used for the procedure that is substituted at least on position by nucleophilically substitutable chlorine, bromine and/or iodine; it is, however, preferable to only use the corresponding chlorine and/or bromine compounds. Particularly preferred is the use of chloroalkanes and/or bromoalkanes, (α ethylene chloride and/or (α-ethyl bromide, (α-chloro and/or (α-bromoketone, (α-chloro

and/or (α-bromocarboxylic acid ester, carboxylic acid chloride and/or bromide, and chlorine and/or bromine aromates and/or heterocycles. With the reaction according to the invention, one or more halogen atoms per molecule are replaced in these starting compounds by fluorine atoms depending on the reaction conditions and ratios.

The essential feature of the invention is the use of hydrofluorides of organic nitrogenous bases as the fluorination agent. The hydrofluorides can be represented by general formula I:

$$B \bullet (HF)_n$$
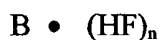
where B is an organic nitrogenous base, and n are whole numbers or fractions of 1-4.

Possible organic nitrogenous B bases are any primary, secondary and/or tertiary amines including N-heterocycles. When formula II is given as the general formula for these amines:

$$R_1R_2R_3N \qquad\qquad (II)$$

the following meanings are provided:

R_1: An alkyl group, preferably with 1-10 and especially with 1-6 C atoms,

A cycloalkyl group, preferably with 5-7 C atoms,

An aralkyl group, preferably with 6-10 C atoms, or

An aryl group preferably also with 6-10 C atoms,

R_2 and R_3: Hydrogen, alkyl, cycloalkyl, aralkyl and aryl groups of the same kind as indicated for R1.

The groups R_2 and R_3 can be the same or different. Two of groups R_1, R_2 and R_3 can also be closed to form a cycloaliphatic ring that may be interrupted by other heteroatoms as well as by O atoms. It is also possible for the three groups R_1, R_2 and R_3 to be part of a heterocyclic ring which results in corresponding N-heterocycles. Preferred organic nitrogenous B bases are primary, secondary and/or tertiary amines with a total of up to 12 C atoms, and the secondary and/or tertiary aliphatic amines are especially preferred.

Concrete examples of B bases are: N-butylamine, N-decylamine diethylamine, di-n-octylamine, trimethylamine, triethylamine, tri-n-propylamine, isopropyldiethylamine, tri-n-butylamine, cyclohexylamine, N-methylaniline, N,N-dimethylaniline, pyrrolidine, piperidine, N-methylpiperidine, morpholine, pyridine, quinoline, etc.

The hydrofluorides I of the nitrogenous B bases are easy to obtain from B bases and hydrogen fluoride; they are substances which are low melting or liquid at room temperature that are particularly resistant to heat; this last property makes it superior to hydrogen fluoride as a fluorination agent since less-reactive substrates can also be easily fluorinated without pressure. Trishydrofluorides can even be distilled in a vacuum without decomposition.

The hydrofluorides are also miscible with most solvents and the substrates to be fluorinated, and they are more reactive than, for example, potassium fluoride. Since they react neutral or at most slightly acid, they practically do not attack borosilicate glass under heat, and they are correspondingly easy and safe to handle. Hence the fluorination reactions with the hydrofluorides can be carried out in equipment made of borosilicate glass.

The procedure according to the invention is described by the following general reaction equation:

$$R\text{-}Hal + B \bullet (HF)_n \longrightarrow R\text{-}F + B \bullet HHal + (n-1)HF$$

R= organic group

n=1-4

Hal = Cl, Br, (J)

The ratio of substrate to fluorination agent must accordingly be theroetically 1:1 (molar ratio). It is, however, preferable to use an excess of fluorination agent up to approx. 50 molar percent, and especially 10-20 percent. It is, however, also possible to use the fluorination agent as a reaction medium, i.e., at a large excess. This procedure is preferred

when the reaction mixture is to be obtained by stirring with the hydrohalogenide as a precipitate. Adding a neutral solvent or diluent such as dibutyl ether, diphenyl ether, dimethyl sulfoxide, sulfolane or diethylene glycol dimethyl ether can also attain this. When a monohydrofluoride is used for the reaction according to the invention (in formula I, $n = 1$), the halogen different from fluorine released in an exchange during the reaction is bonded in the form of amine hydrohalogenide.

When an amine hydrofluoride I is used when $n > 1$, $(n-1)$ moles hydrogen fluoride arises over the course of the reaction. It is hence useful in this case to add at least the amount of additional amine that would be sufficient to re-complex the freed hydrogen fluoride during the reaction. It is hence possible after adding additional substrate to exploit nearly all of the hydrogen fluoride used over the course of the reaction.

A preferred variation of the procedure for binding the hydrogen fluoride freed during the reaction is to carry out the reaction in the presence of a solvent with sufficient basicity. This variation is above all preferred when it is possible to react the substrate or the product with free nitrogenous base B.

Possible solvents with sufficient basicity are in particular acid amides of which lactams and N-alkyl-substituted lactams and especially N-(C_1C_4)-alkyl-substituted C_5- and/or C_6-lactams are preferred. Examples of such lactams and N-substituted lactams are pyrrolidone, caprolactam, N-methyl pyrrolidone, N-propyl pyrrolidone, N-methyl caprolactam, etc.

The obtained acid amide/hydrogen fluoride mixture can be distilled in a vacuum undecomposed over a wide concentration. They can be freed from dissolved amine hydrohalogenide, titrated with lye, and reused after adding the calculated amount of amine.

The sequence for adding the reactants can be selected as desired depending on considerations of utility. It is not absolutely necessary to use the fluorinating agent as a finished base/hydrogen fluoride complex. It may also be generated in situ during the reaction. In this variation of the procedure, amine is dripped into a mixture consisting of solvent, hydrogen fluoride and the substrate. If the cited acid amides are used as the solvent, this reaction can also be carried out in borosilicate glass.

The reaction temperature is approx. -10 to +150°C depending on the reactivity of the substrate. The length of the reaction also depends on the reactivity of the substrate. The end of the reaction can be easily determined in reactions where the product can be continuously distilled off. In other cases, information on the stage of the reaction can be gained by determining the split-off halogen ions by argentometry. The reaction preparation is processed in a familiar manner, i.e. by distillation, extraction, etc.

The procedure according to the invention is particularly notable in that the fluorination agents can be made easily and cheaply and are safe to handle so that the reactions can be carried out in equipment made of borosilicate glass. In addition, the fluorinating substances of the invention allow the reaction times to be much shorter than in state of the art procedures. The conditions are milder, and the yields are higher.

It was not at all obvious to use organic nitrogenous bases as the fluorinating agent according to the invention since the only (mono)hydrofluoride of a nitrogenous base known to be a fluorination agent, i.e., ammonium fluoride (NH4F), has very slight fluorinating activity. One would suspect that there were no fluorinating substances among the hydrofluorides of nitrogenous bases. It was all the more surprising as we pursued this unobvious path according to the invention when we found that hydrofluorides of organic nitrogenous bases were nonetheless excellent fluorinating agents.

The tetraalkylammonium fluorides known to be fluorinating agents are not hydrofluorides and are accordingly outside of the scope of the invention.

The following examples will further explain the procedure of the invention:

Example 1:

217 g (1.0 mole) 2H-perfluor-n-propyl-chloromethyl ether, $CF_3CHFCF_2OHC_2Cl$, and 15.6 (1.3 mole) triethylamine hydrofluoride were stirred for 8 h at 90°C in a flask with a stirrer, thermometer, reflux cooler and drying pistol. The hydrofluoride dissolved upon being heated. After 1.5 h, triethylamine hydrochloride began to precipitate. After the reaction, the distillable components were distilled out of the reaction vessel from the precipitated salt via a 50 cm long Vigreux column. BP: 66-68°C.

Yield: 120 g $CF_3CHFCF_2OCH_2F \cong 60\%$ of theoretical yield.

Example 2a:

A mixture of 217 g (1.0 mole) 2H-perfluor-n-propyl-chloromethyl ether, $CF_3CHFCF_2OHC_2Cl$, and 137 g (1.3 mole) piperidine hydrofluoride was heated with the exclusion of moisture in a flask with a stirrer, thermometer, and 80-cm-long Vigreux column with a reflux cooler so that 2H-perfluor-n-propyl-fluoromethyl ether (BP: 66-68°C) could be continuously be removed. The reaction ended after 6 h.

Yield: 129 g $CF_3CHFCF_2OCH_2F \cong 65\%$ of theoretical yield.

Example 2b: (comparative example with potassium fluoride)

216.5 g (1.0 mole) 2H-perfluor-n-propyl-chloromethyl ether, $CF_3CHFCF_2OHC_2Cl$, was boiled with 87 g (1.5 mole) dry potassium fluoride in 400 ml N-methyl-pyrrolidone for 10 h with the exclusion of moisture with reflux. After the mixture was cooled to RT, it was poured into water, the organic phase was separated and dried with sodium sulfate. Distilling the product with a 50-cm-long packed column with 4 mm Raschig rings yielded 48 g (24% of theoretical yield) fluoromethyl ether, $CF_3CHFCF_2OHC_2F$, BP: 68-69°C.

Example 3:

1-chlor-2,2,2-trifluoroethyl methyl ether, $CF_3CHClOCH_3$, to form 1,2,2,2-tetrafluoroethyl methyl ether, $CF_3CHFOCH_3$.

BP: 37-38°C, yield: 1152 g $CF_3CHFOCH_3$ $\cong$ 80% of theoretical yield.

Example 7:

92 g (0.5 mole) 1-chlor-2,2,2-trifluoroethylchloromethyl ether, $CF_3CHClOCH_2Cl$, and 97 g (0.8 mole) triethylamine hydrofluoride in a flask with a stirrer, thermometer, reflux cooler and drying pistol was stirred for 10 h at a 90°C bath temperature. After 15 min., triethylamine hydrochloride started to precipitate out of the homogenous solution that arose after being heated. The distillation of the reaction product produced 67 g 1-chlor-2,2,2-trifluoroethyl fluoromethyl ether, $\cong$ 80% of theoretical yield, BP: 63°C.

Example 8:

183 g (1.0 mole) 1-chlor-2,2,2-trifluoroethyl chloromethyl ether, $CF_3CHClOCH_3$, and 137 g (1.3 m mole) piperidine hydrofluoride were heated in a distillation apparatus with a stirrer and an 80-cm-long Vigreux column (the internal temperature rose from 75 to 110°C) so that 1-chlor-2,2,2-trifluoroethyl fluoromethyl ether, $CF_3CHClOCH_2F$, BP: 62-63°C could be removed.

Yield: 117 g $CF_3CHClOCH_2F$, $\cong$ 70% of theoretical yield.

Example 9:

310 g (1.7 mole) 1-chlor-2,2,2-trifluoroethyl chloromethyl ether, $CF_3CHClOCH_2Cl$, 274 g (2.6 mole) piperidine hydrofluoride, and 300 ml xylene were heated in a distillation apparatus with a stirrer and an 80-cm-long Vigreux column with the exclusion of moisture (the internal temperature rose from 105 to 125°C) so that 1-chlor-2,2,2-trifluoroethyl fluoromethyl ether could be continuously removed.

Yield: 182 g $CF_3CHClOCH_2F$, $\cong$ 65% of theoretical yield. BP: 63-64°C.

Example 10:

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130 g (0.7 mole) 1-chlor-2,2,2-trifluoroethyl chloromethyl ether ($CF_3CHClOCH_2Cl$) and

188 (1.8 mole) piperidine hydrofluoride were stirred for 5 h at 130°C in a 500 ml steel

autoclave with a lift-thrust stirrer. The pressure rose to a maximum 5 bar. The

distillation of the reaction product through an 80-cm-long Vigreux column produced 48 g

1,2,2,2-tetrafluoroethyl fluoromethyl ether ($CF_3CHFOCH_2F$), BP: 43°C, which

corresponds to a conversion of 47%, and 37 g 1-chlor-2,2,2-trifluoroethyl fluoromethyl

ether ($CF_3CHClOCH_2F$), BP: 63°C which corresponds to a conversion of 32%.

Example 11:

N-butylfluoride was continuously distilled off from a solution kept at 90-100°C of 157 g

(1.3 mole) triethylamine hydrofluoride and 137 g (1.0 mole) n-butyl bromide in 100 ml N-

methylpyrrolidone in a distillation apparatus with a 50-cm-long Vigreux column while

stirring, BP: 31-32°C.
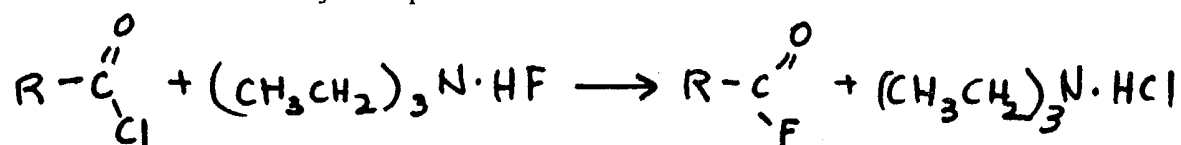
Yield: 37 g n-C_4H_9F $\cong$ 65% of theoretical yield.

Example 12:

A mixture of 122.5 g (1.0 mole) chloroacetic acid ethyl ester and 157 g (1.3 mole)

triethylamine hydrofluoride was stirred for 3 h at 80°C with the exclusion of moisture.

Then the product was distilled off via an 80-cm-long Vigreux column, BP: 79-80°C/200

Torr.

Yield: 74 g $FCH_2\text{-}COOC_2H_5$ $\cong$ 70% of theoretical yield.

Examples 13 a-c:

Reaction of Chlorocarbonyl Compounds

$$R-\overset{O}{\overset{\|}{C}}{\diagdown}_{Cl} + (CH_3CH_2)_3N\cdot HF \longrightarrow R-\overset{O}{\overset{\|}{C}}{\diagdown}_F + (CH_3CH_2)_3N\cdot HCl$$

R	BP (°C)	Yield (% of theoretical)
a) C_6H_5	157	70
b) CF_2Cl	-21 to -19	70
c) OCH_2CH_3	54-56	75

Triethylamine hydrofluoride was suspended in N-methylpyrrolidone in a flask with a stirrer, thermometer, dropping funnel, and a column with a column head. The chlorocarbonyl compound was added to the suspension at 15-20°C, and then all volatile components were distilled off in a vacuum. The obtained distillate was redistilled.

Example 14:

119 g (0.8 mole) 1-chlor-2,2,2-trifluoroethyl methyl ether, $CF_3CHClOCH_2F$ was added dropwise to a solution of 140 g (1.1 mole) N-methylaniline hydrofluoride in 300 ml N-methylpyrrolidone in a distillation apparatus with an-80-cm long Vigreux column, stirrer, thermometer and dropping funnel at 135-145°C. The arising 1,2,2,2-tetrafluoroethyl methyl ether, ($CF_3CHFOCH_3$), was continuously distilled off. The reaction time was 4 h. 81 g of the distillate was obtained, BP: 38-43°C. Redistillation through an 80-cm-long Vigreux column yielded 61 g $CF_3CHFOCH_3$ and 15 g starting product. Taking into consideration the recovered amount of ether, this corresponds to 70% of the theoretical yield.
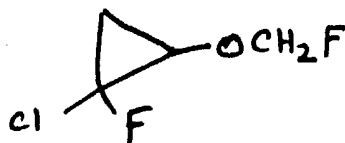
Example 15:

A mixture of 184 g (1.14 mole) triethylamine-tris-hydrofluoride and 137 g (1.0 mole) bromoacetone was heated to 110-114°C at 260-270 bar in a stirrer made of borosilicate glass. When fluoroacetone started to develop, 67 g triethylamine (0.66 mole) was added dropwise so that only a slight amount entered the gas-filled area above the reaction mixture which remained continuously slightly acidic. The fluoroacetone was continuously distilled through a column with Raschig rings into a cooled receptacle. Then 200 ml dry diglyme and 91 g (0.66 mole) bromoacetone was added to the reaction mixture, and the fluoroacetone was distilled off in a vacuum. During this period, another 51 g (0.5 mole)

triethylamine was slowly added dropwise. 125 g of a nearly 87% crude product was obtained that yielded 81 g fluoroacetone with a boiling point of 78°C after drying on magnesium sulfate and distillation.

Yield: 64% of theoretical yield.

Example 16:

A mixture of 47.5 g 2-fluor-2-chlorocyclopropylchloromethyl ether (0.3 mole), 24.5 tri-n-butylamine-tris-hydrofluoride and 37 g tributylamine (0.2 mole) was slowly heated in a vacuum to 80-100°C. 31 g of an approx. 93% product was distilled off at a head temperature of 40°C with a rising vacuum of 100-30 mbar which corresponds to 68% of the theoretical yield. The product was a mixture of two diastereomers at a ratio of approx. 1:4 with a boiling point of 35°C at 40 mbar. The product was identifiable as 2-fluor-2-chlorocyclopropylfluoromethyl ether according to the analysis and nuclear resonance spectra:

Example 17:

A mixture of 2,4-dinitrobromobenzene (1.0 mole), 64 g triethylamine-tris-hydrofluoride (0.4 mole) and 81 g triethylamine (0.8 mole) was heated to 130°C while stirring. After 1 h, titration of a sample yielded a content of bromine ions that was 87% of the theoretical yield. After cooling, the reaction mixture was extracted several times with ether, and the ether phase was processed by distillation.

Yield: 69 g (74 % of theoretical) 2,4-dinitrofluorobenzene with a boiling point of 120°C at 0.04 mbar; the product was uniform according to a thin-layer chromatogram.

Example 18:

120 g triethylamine-tris-hydrofluoride (0.75 mole) was added dropwise to a solution of 46 g 2,4,6-trichloropyrimidine (0.25 mole) in 300 g dry N-methylpyrrolidone at RT. The

mixture was then slowly heated for 5 h to 90°C and then processed by distillation. 22 g (66% of theoretical yield) 2,4,6-trifluoropyrimidine, BP: 97-102°C was obtained.

Example 19:

A solution of 46 g cyanuric chloride (0.25 mole) in 600 ml N-methylpyrrolidone was added to a stirrer made of borosilicate glass, and 120 g distilled triethylamine trishydrofluoride (0,75 mole) was added dropwise. A temperature of approx. 20°C was maintained by occasionally cooling. A gradually thickening precipitate arose of triethylamine hydrochloride. After subsequently stirring for 30 min., the flask was connected to a descending condenser and a subsequent cold trap in a dry-ice bath, an oil pump vacuum was applied, the reaction mixture was slowly heated to a max. 80°C, and the liquid component of the reaction mixture was distilled off as much as possible. The receiver then held 500 g of a solution of 0.9 mole HF in N-methylpyrrolidone that was used after adding 0.3 mole triethylamine for the next setup as a fluorination agent. 30 g crude cyanuric fluoride was in the cold trap from which 28 g pure product (83% of theoretical yield), BP: 73°C was obtained after redistillation.

Example 20:

2 kg of a solution of 300 g HF (15 mole) in N-methylpyrrolidone was added to a 4-liter stirrer made of borosilicate glass with a descending cooler, a 2-liter receiver and subsequent cold trap in a dry ice bath; 300 g (1.63 mole) cyanuric chloride was dissolved in it (1.63), then 500 g triethylamine (5 mole) at 20-25°C was added dropwise over approx. 2 h with occasional cooling with ice water. A gradually thickening precipitate immediately arose of triethylamine hydrochloride. The mixture was stirred for 30 min., an oil pump vacuum was applied, the mixture was heated slowly to a max. 80°C, and the liquid components of the reaction mixture were distilled off as much as possible. The receiver then contained approx. 1.4 kg of a solution of 140 g HF (7 mole) in N-methylpyrrolidone; in the cold trap was 205 g crude cyanuric fluoride from which 200 g (91% of theoretical yield) of pure product with a boiling point of 73°C was obtained after redistillation.

The distilled solution of hydrogen fluoride in N-methylpyrrolidone was used for the next preparation after replacing the used amount. Diluted caustic soda was added to the distillation residue in the flask until a clearly alkaline reaction occurred. A nearly solid-free diphase mixture arose from which the lighter triethylamine was removed. 450 g was obtained which was reused after being dried.

Example 21:

92 g cyanuric chloride (0.5 mole) was dissolved in a mixture of 600 g N-methylpyrrolidone and 90 g hydrogen fluoride (4.5 mole). Then 278 g tributylamine (1.5 mole) was added dropwise at 20-30°C. Toward the end, the reaction solution became slightly cloudy from precipitating hydrochloride. At 1 mbar and a head temperature of 61°C, 60 g crude cyanuric chloride collected in the cold trap, and 543 g N-methylpyrrolidone with 3.1 moles HF collected in the receptacle. 92% of the theoretical yield of tributylamine was obtained from the residue in the flask. The crude cyanuric chloride was redistilled.
Yield: 55 g (81.5% of theoretical yield), BP: 73°C.

Example 22:

Using the same setup as in example 21, 195 g N-ethyl-diisopropylamine (1.5 mole) was added dropwise as the amine component. The described distillation yielded 538 g N-methylpyrrolidone with 2.4 mole HF and 64 g crude cyanuric fluoride. After redistillation, 58 g (86% of theoretical yield) resulted. 85% of the amine was recovered.

Example 23:

Using the same setup as in example 21, 149 g N-methylpiperidine (1.5 mole) was added as the amine component. The described distillation procedure yielded 527 g N-methylpyrrolidone with 2.9 mole HF and 58 g cyanuric fluoride (86% of theoretical yield).

Example 24:

44 g cyanuric fluoride (0.24 mole) was dissolved in a mixture of 275 g N-methyl

caprolactam and 42 g hydrogen fluoride (2.15 mole). At 25°C, 73 g triethylamine (0.72

mole) was added dropwise. By applying an oil vacuum and heating the reaction mixture

to 70°C, 25 g cyanuric fluoride (77% of theoretical yield) was obtained in the cold trap.

Example 25:

53 g cyanuric chloride (0.29 mole) was dissolved in a mixture of 329 g -caprolactam and

52 g hydrogen fluoride (5.2 mole). At 20°C, 87 g triethylamine (0.87 mole) was added

dropwise. By applying an oil vacuum and heating the mixture to 70°C, 13 g cyanuric

fluoride (33% of theoretical yield) was obtained.

Example 26.

120 g triethylamine-tris-hydrofluoride (0.75 mole) was dripped into a solution of 46 g

cyanuric chloride (0.25 mole) in 285 g N-n-propylpyrrolidone at 20°C. By applying an oil

vacuum and heating the mixture to 70°C, 25 g (74% of theoretical yield) cyanuric fluoride

was obtained in a cold trap.